

SUMMARY OF IMPORTANT IDEAS FROM CHEMISTRY 350 (TEXT: LOUDON, "ORGANIC CHEMISTRY," 4TH ED.)

FORMAL CHARGES ON ATOMS (SECTION 1.2)

For any molecule: to determine whether a given atom is neutral or charged, do the following:

- (1) Count the total number of valence shell electrons surrounding that atom. In most instances there should be eight, although exceptions do exist: for example, hydrogen in any molecule has only two; boron in BF_3 has only six; sulfur, phosphorous, and other second- and third-row elements can have more than eight, as in PCl_5 and so on.
- (2) Count the number of valence shell electrons specifically belonging to the atom in question. To do this, you count all of non-bonding electrons on the atom **plus one electron** from each two-electron covalent bond that the atom makes. If this number is the same as the number of valence shell electrons of the neutral atom (1 for H, 3 for B, 4 for C, 5 for N, 6 for O, etc.), there is no charge; if it is different, the atom will be charged.

Examples

Carbon:

- (a) CH_4 has eight electrons around carbon, two from each bond; of these eight, four belong to C and the other four belong to the hydrogens, one per H. Since neutral C has four valence shell electrons and neutral H has one, there are no charges on any of the atoms of CH_4 .
- (b) $^+\text{CH}_3$ has only six electrons around carbon, and is therefore quite unstable. Of these six, three belong to C; because this is one fewer than the number that a neutral C would have, this C has unit positive charge.
- (c) $\cdot\text{CH}_3$ has seven electrons surrounding carbon, of which four specifically belong to C; the central atom of the methyl radical is, therefore, uncharged.
- (d) $^-\text{:CH}_3$ has an octet of electrons around carbon. Five of these (the non-bonding electron pair plus one from each C-H bond) belong to C. Because this is one more than the number of valence electrons needed for a neutral C, the central atom has unit negative charge.

Oxygen:

- (a) In water, oxygen is surrounded by eight electrons of which six (the two non-bonding pairs plus one electron from each bond) specifically belong to it. The atom is uncharged because neutral O has six valence shell electrons. $\text{H}-\ddot{\text{O}}-\text{H}$
- (b) In hydroxide ion, there are again eight electrons around O, but now seven specifically belong to it; the atom has unit negative charge. $\text{H}-\ddot{\text{O}}:^-$
- (c) In hydronium ion, there are again eight electrons around O, but now only five specifically belong to it; the atom has unit positive charge. $\begin{array}{c} \text{H}-\overset{+}{\text{O}}-\text{H} \\ | \\ \text{H} \end{array}$
- (d) The species to the right is very unstable with only six electrons surrounding O; since five specifically belong to O, the atom has unit positive charge. $\text{H}-\overset{+}{\text{O}}:$

Nitrogen:

Convince yourselves that the species to the right have the charges shown. Note that ion (b) corresponds to the addition of H^+ to H_3N : using the unshared electron pair on N for the covalent bond. Note also that (c) and (d) correspond to removal of one and two protons, respectively, from H_3N : – for each proton removed, an extra unshared pair of electrons is left on N.

a. H_3N : b. $\text{H}_4\overset{+}{\text{N}}$

c. $\text{H}_2\ddot{\text{N}}:^-$ d. $\text{H}-\overset{-}{\text{N}}:$

LEWIS BASE/LEWIS ACID REACTIONS (SECTIONS 3.1 - 3.3)

The great majority of organic reactions can be understood within the framework of attack by a **Lewis Base** (or **nucleophile**) on a **Lewis Acid** (or **electrophile**). Thus, any understanding of organic reactions (no matter how simple or complex) rests on a clear appreciation of Lewis Base/Lewis Acid reactions. **NO SUBJECT IS MORE IMPORTANT FOR MASTERING ORGANIC REACTIONS AND THEIR MECHANISMS.**

Definitions:

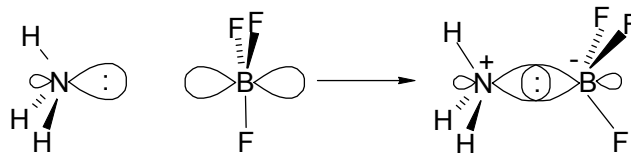
1. A **Lewis Base** (or **nucleophile**) is a species having an electron pair available for sharing.
2. A **Lewis Acid** (or **electrophile**) is a species that can accept a share in a pair of electrons. It has an "empty orbital"* (or its equivalent) for accepting the electron-pair delivered by the Lewis Base.
3. A **Lewis Base/Lewis Acid reaction** involves the formation of a two-electron covalent bond using a pair of electrons supplied by the base.

*The phrase "empty orbital" is put in quotation marks because it is a misnomer. An orbital is merely the region of highest probability for locating electrons. If there are no electrons, there is (obviously) no orbital. Nevertheless, the terminology is widely used, and it will be used from here on without apology and without quotation marks.

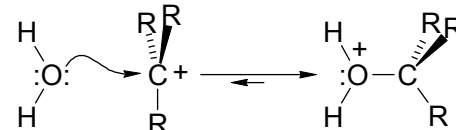
4. The curved arrow notation (review Sections 3.1-3.3 and Study Guide Links 3.1-3.3 in the *Study Guide*) shows the direction of flow of a pair of electrons from the electron-rich Lewis Base to the electron-poor Lewis Acid.

Examples:

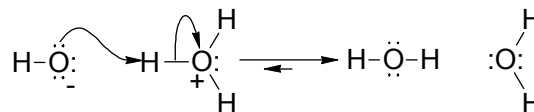
1. Boron, with an empty p-orbital and surrounded by only six electrons, is electron-poor – BF_3 is, therefore, a prototypical Lewis Acid. In H_3N :, nitrogen is electron-rich – it has an electron-pair available for sharing. Thus, the Lewis Base H_3N :, supplies the pair of electrons to form the covalent bond that is found in the product. Note that B's hybridization changes from sp^2 to sp^3 , whereas N's remains unchanged at sp^3 . Note also that the product, although neutral, cannot be written without formal plus and minus charges; you should convince yourselves that the charges are correct, as written. Finally, note the use of the curved arrow, showing the flow of a pair of electrons from the Lewis Base to the Lewis Acid, resulting in the formation of a covalent bond.



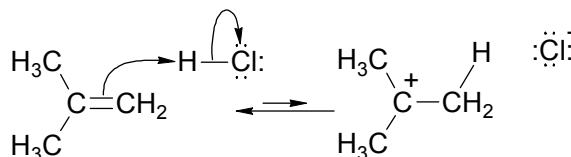
2. This step (found in the dehydration of alcohols, the hydration of alkenes, the $\text{S}_{\text{N}}1$ hydrolysis of alkyl halides, etc.) involves attack of a Lewis Base (water) on a Lewis Acid (the carbocation). In the course of the reaction, positive charge is transferred from C to O; note that the overall charge is the same on both sides of the equation.



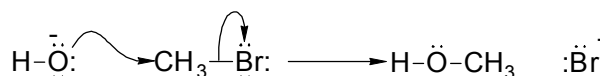
3. This reaction, neutralization of an acid by a base, is different from examples 1 and 2 in the sense that hydronium ion is not, strictly speaking, an electron-deficient species. Although this would ordinarily be called a Brønsted-Lowry acid/base proton transfer, it can also be viewed within the framework of Lewis reactions – that is, hydronium ion is the source of a proton H^+ which is electron-deficient in exactly the way that BF_3 (example 1) or the carbocation (example 2) were. Thus, the Lewis Base hydroxide has attacked the Lewis Acid H^+ . As above, note that charges on the two sides of the equation are the same.



4. This reaction, the first step in the Markownikoff addition of H-Cl to an alkene, uses the π -electrons of the alkene to attack the Brønsted-Lowry acid. Note that the charges on both sides of the equation are the same. This reaction can be viewed as electrophilic attack by H^+ on the alkene or as nucleophilic attack by the alkene on H-Cl .

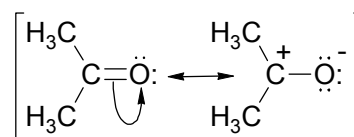
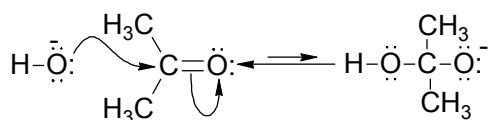


5. As with hydrogen in the proton-donating species in examples 3 and 4, the methyl group, here, is not (strictly speaking)



electron-deficient. Nevertheless, this S_N2 reaction is a Lewis Base/Lewis Acid reaction – it is (in a sense) the transfer of a methyl cation, H_3C^+ , from Br^- to HO^- , just as example 3 was the transfer of H^+ from H_2O to HO^- .

6. This step (from the base-catalyzed hydration of acetone, Chapter 19, later this semester) is like examples 3, 4, and 5 in that acetone is not (strictly speaking) an electron-deficient molecule. There are two (relatively equivalent) ways of viewing this reaction within the context of Lewis Base/Lewis Acid chemistry: (a) HO^- is performing a displacement reaction on the π -electrons of the double bond (just as it can displace σ electrons in example 5) – thus C in the carbonyl group acts as an electron-deficient Lewis Acid; (b) one can think of acetone in terms of its minor dipolar resonance contributor (shown in brackets) in which the carbon is clearly an electron-deficient atom.

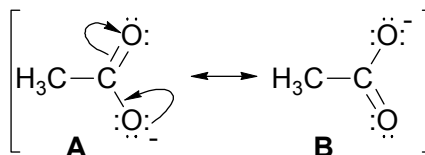


DRAWING RESONANCE STRUCTURES

A basic principle of resonance theory is that whenever electrons can be delocalized (that is, whenever more than one structure can be written for a molecule without violating the rules of bonding), the true molecule is more stable than any one of the individual localized structures would imply. In nearly every case, one resonance contributor can be generated from another by two-electron shifts of either π -electrons or non-bonding electrons. Carefully review Sections 1.4 and 15.6 as well as SGL 15.3.

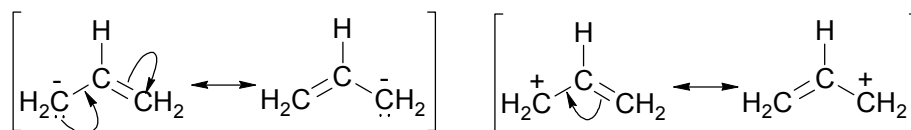
Examples:

1. Acetate ion (Sections 1.19 and 6.10) – Structures **A** and **B** contribute equally to the true structure. The true structure is a resonance hybrid of contributors **A** and **B**. Starting with **A**, one can generate **B** by moving a pair of non-bonding electrons from the negatively charged oxygen, forming a π -bond between O and C; simultaneously, a pair of π -electrons is shifted to the other oxygen which develops negative charge. The



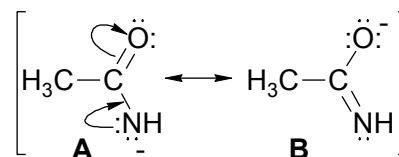
curved arrow notation is a convention that is used to show the direction of flow of an electron-pair. Note that (as was true for Lewis Base/Lewis Acid reactions) the head of the arrow shows the ultimate placement of the electron-pair. The curved arrow is nothing more than a bookkeeping device for keeping track of electrons and their positions. The **double-headed arrow** between **A** and **B** is a symbol that is used **ONLY** to signify resonance - it is not the same as a pair of equilibrium arrows because resonance is not a chemical reaction. In contrast to chemical equilibrium between real species, the resonance contributors are "imaginary" species – hence the use of the special symbol, the double-headed arrow.

2. Allyl anion and cation (Chapters 15 and 17) – As with acetate ion, the curved arrow shows



the flow of an electron pair from the negatively charged carbon (allyl anion) or to the positively charged carbon (allyl cation). As with acetate ion, the two structures contribute equally for both of these charged species. Note, also, the different directions of electron flow, as shown by the curved arrows: from left to right in the anion, from right to left in the cation.

3. Conjugate base of acetamide (Chapter 21) – Although formally like acetate ion, the two structures here do not contribute equally to the resonance hybrid. Because structure **B** has negative charge on O, a more electronegative atom than N, the true molecule resembles **B** more than it does **A**. **B** is the major contributor to the structure.



4. Carbon dioxide - **B** and **C** contribute equally to the resonance hybrid, but their contribution is probably less than **A**'s for three reasons: (a) **B** and **C** have one less bond than **A**; (b) **B** and **C** have separation of charge; (c) **B** and **C** have a carbon that is
-
- surrounded by only six electrons. In general, it costs energy to have (a) fewer bonds, (b) separated charges, and (c) less than an octet of electrons – because **A** avoids all of these, its contribution is greatest. **D** and **E**, like **B** and **C**, also contribute equally – their contribution is less than **A**'s because of charge separation, but probably greater than that of **B** and **C** because of the greater number of bonds and no atom with fewer than eight electrons.

5. Reaction intermediate from bromination of benzene (Section 16.4) – **A** and **C** contribute equally to the true structure of the molecule. **B**'s contribution must be different (since its structure is different) but it is certainly comparable to that of **A** and **C** (all three structures have the same number of bonds and all have positive charge on a carbon atom). Note that as in all electrophilic aromatic substitution intermediates, positive charge is on those carbons that are ortho and para to the point of attack.
-

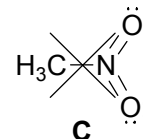
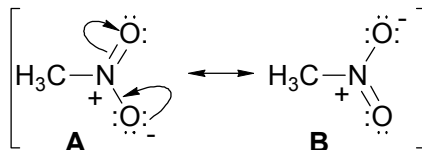
In drawing resonance structures, there are various pitfalls to avoid:

1. All structures must have the same total charge. In carbon dioxide (for example), each structure is neutral overall, even though **B** through **E** have charged atoms.
2. Every structure must have the same total number of electrons. Obviously, if you write a structure with more electrons or fewer electrons than exist in another, you are no longer

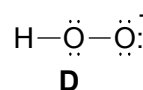
talking about the same molecule.

3. One must not violate the octet rule by having more than eight electrons about a first-row element. For example, nitromethane is represented by equal contributions from structures **A** and **B**. Structure **C** is not a

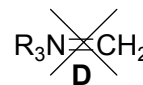
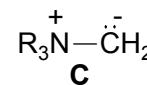
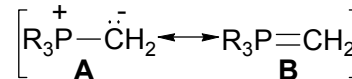
correct structure because N has 10 electrons around it. Note that even though nitromethane is a neutral molecule, it is impossible to write a structure without



charged atoms. Similarly, the conjugate base of hydrogen peroxide is represented only by structure **D**; structure **E**, obtained by a two-electron shift from right to left, is invalid because the central atom is surrounded by 10 electrons.



4. In contrast to the examples discussed above, it is permissible to violate the octet rule for elements in the second-row (or higher). These elements have low-lying orbitals (such as 3d for S and P) available into which "excess" electrons can be placed. Thus, structures **A** and **B** are both valid for the Wittig reagent (Section 19.13). In contrast, only **C** is valid for the related ylide in which N (a first-row element) takes the place of P.



5. The p-orbitals on individual atoms must be parallel in order for π -overlap to be possible. Also, a single atomic geometry must accommodate all electronic motion in the various contributors. [Examples of both of these ideas will be presented in lecture.]